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Electrochemical aspects of the Hybrid Sulfur Cycle for large scale hydrogen production

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ABSTRACT

The Hybrid Sulfur Cycle is a thermo-electrochemical process designed for the large scale production of hydrogen. The two-step process is essentially based on water splitting using various sulfur species as intermediates. The limiting step in the overall process is the electrochemical oxidation of sulfur dioxide to form sulphuric acid, which suffers from a substantial (~0.4 V) anodic overpotential. Here we report on various aspects of sulfur dioxide oxidation in an acidic media including the effects of electrode preconditioning, the electrode substrate and electrolyte effects, the combination of which has allowed development of a sulfur dioxide oxidation mechanism which is described and discussed. Additionally, the electrochemical oxidation of sulfur dioxide has been shown to be an oscillating reaction, which is also a novel finding.

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Introduction

The electrochemical oxidation of sulfur dioxide in aqueous solutions is of industrial importance. The mechanism of the oxidation reaction has been extensively studied for application to the hybrid sulfur (HyS) cycle [1–6], a thermochemical cycle for hydrogen production also referred to as the Westinghouse cycle. Other applications include the removal of sulfur dioxide from chemical exhaust gases (flue gas desulfurisation) [7–13], electrogenerative oxidation [14,15] and the analytical determination of sulfur dioxide concentrations [16,17]. Many aspects of the reaction are also of interest regarding fundamental electrocatalysis [18–25] and the electrochemistry of sulfur dioxide has been a topic of renewed interest in recent years due to its relevance in

proton exchange membrane fuel cell (PEMFC) applications [26,27].

The Hybrid Sulfur Cycle

Thermochemical water splitting cycles are a possible enabling technology for the hydrogen economy. Sulfur based cycles in particular have been extensively studied due to their high thermal efficiencies and large scale hydrogen production potential (>100,000 kg H₂ year⁻¹) [28].

The HyS cycle is a hybrid thermo-electrochemical cycle which incorporates the use of sulfur oxide based intermediates to split water with high efficiency (>40% based on lower heating value (LHV) hydrogen [29–32]). Energy inputs can potentially be provided exclusively by solar energy [33–35], although the cycle was originally envisaged to be

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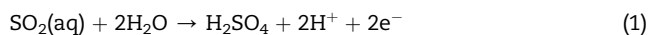
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driven by a nuclear heat source [36,37]. Thermal energy is used to decompose sulphuric acid, while electrical energy is supplied to an acid electrolyzer. Research into the cycle is currently focused on flow sheeting and cycle integration [30–33], economic analysis and feasibility [28,33–35,38], the efficient separation of sulfur dioxide and molecular oxygen [39], the thermal decomposition of sulfur trioxide [40], and optimisation of the electrolysis step [41–44].

The acid electrolyzer is unique to the HyS cycle and has been identified by Jeong and Kazimi [32] as the main source of inefficiency within the cycle – a drop of 3% of the required electrolyzer voltage was predicted by the authors to result in about a 1% gain in cycle efficiency. From an economic point of view, optimization of the electrolyzer is important since, at current performance (current density 200 mA/cm²), the electrolyzer has been estimated at more than 50% of the total plant cost [32].

The original electrolyzer design concept consisted of two compartments separated by a membrane, somewhat similar to early fuel cell constructions. Dissolved sulfur dioxide is oxidized to sulphuric acid (Eqn. (1)) in the anode compartment, while evolution of hydrogen (Eqn. (2)) occurs at the cathode; i.e.,



More modern electrolyzer designs include the use of a membrane electrode assembly (MEA) [43] which gives a reduced overall cell resistance.

The current density a cell is capable of producing at a specified voltage is dependent on several factors including the composition and concentration of anolyte and catholyte, as well as the applied temperature and pressure. A current density of 200 mA/cm² was reportedly achieved by Westinghouse in early development of the electrolyzer [45], and a performance goal of 500 mA/cm² was specified. An improvement of this magnitude would result in a 60% decrease in the required electrolyzer area and significantly reduce electrolyzer capital cost [32]. The target optimal electrolyzer performance proposed by Gorenssek and Summers involved a current density of 500 mA/cm² for an applied voltage of 0.6 V [46]. This performance was reportedly achieved by Staser et al. [44] for a gaseous sulfur dioxide feed, although best performance with dissolved sulfur dioxide has not exceeded the original target of 200 mA/cm² for an applied potential of 0.6 V [47].

Technical challenges for the HyS cycle

Challenges for construction and operation of the electrolyzer are mainly related to sulfur dioxide cross over, mass transfer issues, materials of construction, catalyst cost and stability, and cell overpotential. Modelling of the HyS cycle has resulted in proposed conditions for the acid electrolyzer including high anolyte acidity and elevated temperatures (50–60 wt% H₂SO₄ and 80–90 °C) [29–32]. These effects are mostly related to the

concentration of active species and basic kinetic effects. Sulphuric acid concentration, however, is a more complicated variable in terms of its effect on reaction kinetics and requires further examination.

Since the oxidation of sulfur dioxide involves protons (Eqn. (1)), it is expected that the reversible potential of the reaction will be affected by the acid concentration through the changing activity of protons in solution; i.e., the Nernst effect. Indeed, Appleby and Pinchon observed that the onset of oxidation occurred at higher potentials for more concentrated sulphuric acid solutions [2]. Colón-Mercado and Hobbs more recently presented experimental evidence for this potential change, showing an increase in the observed open circuit potential (OCP) with increasing acid concentration [48].

Sulphuric acid concentration may also have the ability to affect reaction kinetics and possibly the reaction mechanism. The experimental results of Struck et al. [49] indicate that the current density decreased dramatically at a potential of 0.7 V vs SHE after increasing the sulphuric acid concentration from 5 to 80 wt%. Lu and Ammon also noted a decline in performance as the acid concentration was increased from 30 to 50 wt% [50], as did Appleby and Pinchon using a rotating electrode in solutions of increasing concentration [2]. This decrease was concluded to result from the decrease in activity of the active species with increasing acid concentration. However, a possible oversight in evaluating the effect of sulphuric acid concentration could be specific to the platinum electrodes used by these authors. Sulphuric acid concentration possibly affects the catalytic state of a platinum electrode since similar electrode preconditioning in acids of different concentrations results in different oxidative behaviour.

In terms of catalysts for the sulfur dioxide oxidation, Appleby and Pinchon tested several different base materials for use as the anodic electrode in highly concentrated sulphuric acid solutions [2], followed by a similar investigation from Lu and Ammon [4]. Using similar solution compositions and temperatures, both authors found carbon materials, including graphite and carbides, to be catalytically inactive for the reaction. Appleby and Pinchon further found activated carbon and carbon black to have only intermediate activity, while both studies suggest the use of catalysed carbon supports for best results. The oxidation behaviour of porous catalysed carbon was also investigated by Wiesener [15]. Treatment of the carbon at high temperatures and under various oxidizing gas streams gave some improvement in performance, as did the addition of a mixed oxide catalyst; however, it was the addition of traces of a noble metal (platinum in this case) that gave the most significant catalysis [15]. Of the noble metal catalysts tested [2,4], Pt was consistently found to have high activity, although the results are somewhat mixed for other noble metals. Palladium showed the best performance in Ref. [4] and the formation of a palladium oxide on the electrode was also suggested to further enhance the reaction. However, more recent results of Colón-Mercado and Hobbs do not support the high activity of palladium compared to platinum [48]. These authors carried out an investigation of electrode activity using platinum and palladium supported on carbon particles (Pt/C and Pd/C). Platinum was found to have comparatively lower activation energy with higher observed current densities. Dissolution of the palladium electrode was

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